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<p>(21) International Application Number: <b>PCT/GB99/00298</b></p> <p>(22) International Filing Date: <b>28 January 1999 (28.01.99)</b></p> <p>(30) Priority Data: 9803249.3      17 February 1998 (17.02.98)      GB</p> <p>(71) Applicant (for all designated States except CA FR US): <b>SOF-ITECH N.V. [BE/BE]; Rue de Stalle 140, B-1180 Brussels (BE).</b></p> <p>(71) Applicant (for FR only): <b>COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER S.A. [FR/FR]; 50, avenue Jean Jaurès, F-92541 Montrouge (FR).</b></p> <p>(71) Applicant (for CA only): <b>SCHLUMBERGER CANADA LIMITED [CA/CA]; Monenco Place, 24th floor, 801 6th Avenue, S.W., Calgary, Alberta T2P 3W2 (CA).</b></p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): <b>BAILEY, Louise [GB/GB]; 58 The High Street, Yelling, St. Neots, Cambridgeshire PE19 4SD (GB). GROVER, Boyd [GB/GB]; 12 Roslin Close, Harwood Park, Bromsgrove, Worcestershire B60 2EZ (GB).</b></p>	<p>(74) Agent: <b>MIRZA, Akram, Karim; Schlumberger Cambridge Research Limited, High Cross, Madingley Road, Cambridge CB3 0EL (GB).</b></p> <p>(81) Designated States: <b>AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: <b>ANTI-ACCRETION ADDITIVES FOR DRILLING FLUIDS</b></p> <div style="text-align: center; margin: 20px 0;"> <math display="block">  \begin{array}{c}  \text{OR}'' \\    \\  \text{O} = \text{P} - \text{R} \\    \\  \text{OR}'  \end{array}  \quad (I)  </math> </div> <p>(57) Abstract</p> <p>Additives for drilling fluids, in particular for water-based drilling fluids are described which when added to the fluid at levels of up to 10 % weight by volume reduces the accretion and bit-balling tendencies of shale cuttings exposed to said fluids. The additives are based on phosphonate chemistry, and are of the general class (I), wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.</p>		

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**Anti-accretion additives for drilling fluids**

This invention relates to anti-accretion additives for drilling  
5 muds.

**BACKGROUND OF THE INVENTION**

Bit-balling and cuttings accretion are problems encountered when  
10 drilling shales, particularly with water-based muds. Shale  
cuttings can adhere to each other and to the bottom hole  
assembly and cutting surfaces of the bit. Gradually a large  
plastic mass builds up which can block mud circulation and  
reduce rates of penetration. There is a "danger zone" of clay  
15 plasticity for balling and accretion, related to the water  
content of the clay or shale, which can be defined in terms of  
the Atterberg limits of soil mechanics. In the dry zone the clay  
has too little water to stick together and it is a friable and  
brittle solid. In the wet zone the material is essentially  
20 liquid like with very little inherent strength and can be washed  
away.- Intermediate to these zones, i.e., in the danger zone,  
the shale is a sticky plastic solid with greatly increased  
agglomeration properties and inherent strength.

25 When cuttings are exposed to conventional water-based muds they  
usually imbibe water and pass rapidly through these different  
zones, eventually dispersing. However recent advances in  
drilling fluid technology have developed highly inhibitive muds  
which appear to reduce the hydration of shale and in doing so  
30 maintain the cuttings in the danger or plastic zone contributing  
to increased accretion and bit-balling. Field experiences with  
glycol, phosphate and silicate muds in particular have shown  
accretion problems.

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US patent 5,639,715 describes additives for bit-balling prevention based on sulphonosuccinate chemistry.

Phosphorus based additives and compound have been used in the oilfield industry mainly for the purpose of enhancing oil recovery from production wells.

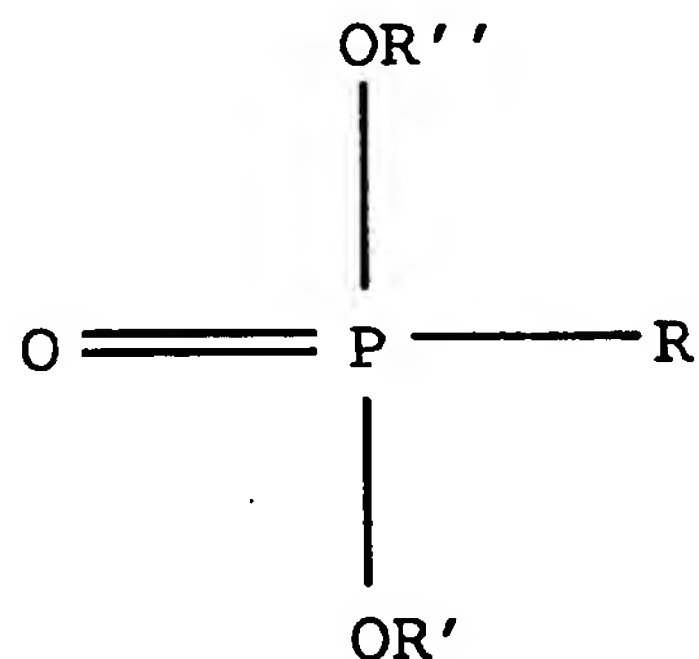
It is the object of the present invention to find alternatives to the known methods of preventing accretion.

10

## SUMMARY OF THE INVENTION

The invention is an additive for drilling mud. The additive reduces the accretion and bit-balling tendencies of cuttings exposed to said muds. The additives are based on phosphonate chemistry, and are preferably of the general class:

(I)



20

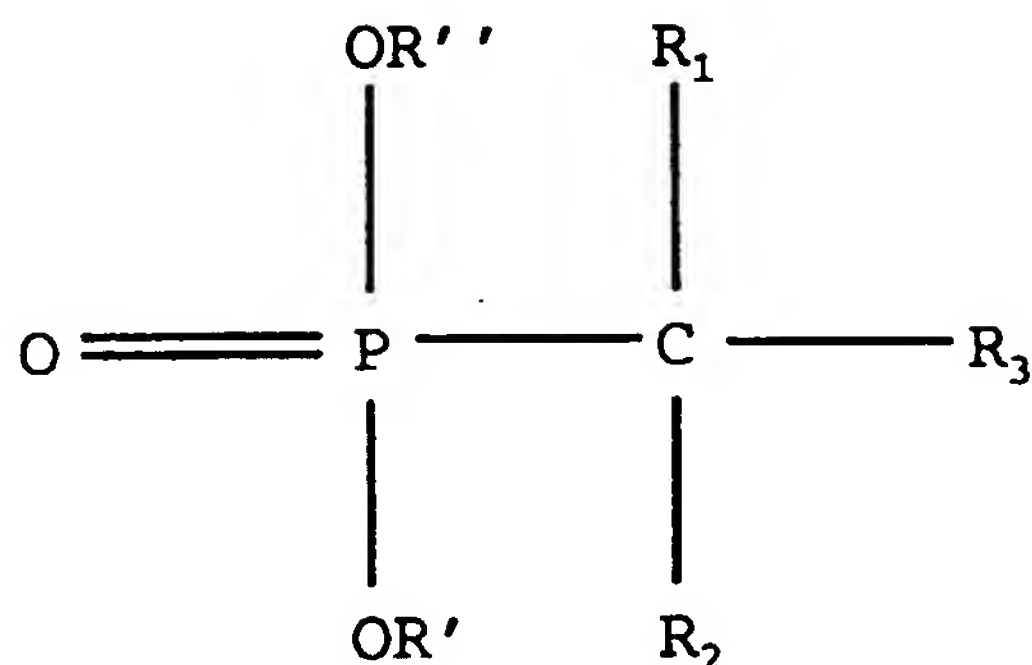
wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

In a more preferred embodiment, the additives are based on the formula

25

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(II)



wherein  $\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are radicals exclusively containing H atoms  
 5 or combinations of H, C, O or P atoms up to a maximum of 100  
 atoms.

In a preferred embodiment of the invention, the additives are  
 containing not more than one phosphor atom.

10

In another preferred embodiment of the invention, the additive  
 is a phosphor derivative of the succinic acid or short chain  
 phosphorylated hydrocarbons.

15 Additives according to the invention are added to the drilling  
 fluid at levels 0.1-10%, preferably 1-5%, weight by volume  
 (%kg/liter). The drilling fluid itself may be oil based, though  
 it is recognized that accretion tends to be less pronounced in  
 drilling muds of this kind. Therefore, the preferred drilling  
 20 fluid in accordance with the present invention is water based,  
 even more preferably a reactive anionic based drilling fluid,  
 such as silicate or phosphate based muds. Further additives as  
 known in the art may be added to impart other desired properties  
 to the mud system. Such known additives include viscosifying  
 25 agents, filtrate reducing agent, and weight adjusting agents.  
 Other preferred additives are shale-swelling inhibitors, such as  
 salts glycol-, silicate- or phosphate-based agents, or any  
 combination thereof.

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These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description below.

5

## MODE(S) FOR CARRYING OUT THE INVENTION

A test used to determine the anti-accretion properties of additives involves squeezing shale or clay cuttings between two  
10 steel plates with a given force causing them to stick to each other and the plates. The force required to slide the plates apart is then determined using a force gauge or spring balance.

Oxford clay cuttings of size 2-4mm were soaked in the test fluid  
15 for 15 minutes. The excess mud was drained from the cuttings using a sieve (500 micron mesh). A small pile of cuttings (5-10g) was put onto the base plate of the tester. The pile was roughly levelled and the top plate replaced over the cuttings. A PTFE spacer was placed on top of the top plate. A screw-mounted  
20 plunger in the tester housing was wound down until it made contact with the spacer. A torque wrench was used to tighten the plunger onto the top plate. The standard torque was 75 inch-pounds (~9N.m). Immediately on reaching this value, the plunger was wound back sufficiently to remove the spacer. A force gauge  
25 or spring balance was then connected to the top plate. The tension on the top plate was then increased by pulling on the force gauge until the plate breaks free from the cuttings bed. The maximum force recorded was the freeing force for the plate or accretion value. Values can range from 1.0 to above 20.0 kg  
30 force.

The phosphonate based additives tested in accordance with the above procedure are added to a water-based mud containing tetrapotassium pyrophosphate (TKPP) and consisting of

35

1000 ml fresh water (base)

- 5 -

85.5 g tetrapotassium pyrophosphate (shale inhibitor)  
2.85 g xanthan gum (viscosifier)  
11.4 g carboxy methyl cellulose of low viscosity grade  
(filtrate reducer)  
5 42.75 g simulated drill solids  
barite (weighting agent) to density 1.08 sg .  
NaOH to pH 9.2  
biocide

10 Baseline accretion values were established as:

Simple polymer mud	5 kg
TKPP mud	21.7 kg

15 The anti-accretion additives were then added to the TKPP mud at levels of 1-5%.

Additives which reduced the accretion value from >10 kg to 9 kg or below were:

20

- Hydrolysed polymaleic acid
- 3-phosphonopropionic acid
- succinic acid
- propyl phosphonic acid

25

- dibutyl-butyl phosphonate
- hydroxyphosphonoacetic acid
- dimethylpropyl phosphonate
- phosphorous acid
- diethyl-ethylphosphonate

30

- ethylmethacrylate phosphate
- tri-ethyl phosphonoacetate
- tetramethyl phosphonosuccinate
- phosphonosuccinic acid
- 2-hydroxyethyl phosphonic acid.

35



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The last five additives (Additives 9-14) were the found most effective. For those the following values were recorded:

<u>TKPP mud + (%)additive:</u>		<u>Accretion value</u>
5		
	1% diethyl-ethylphosphonate	8 kg
	5% diethyl-ethylphosphonate	7 kg
	5% ethylmethacrylate phosphate	6 kg
	1% tri-ethyl phosphonoacetate	8 kg
10	5% tri-ethyl phosphonoacetate	5 kg
	5% tetramethyl phosphonosuccinate	7 kg
	5% phosphonosuccinic acid	7 kg
	5% 2-hydroxyethyl phosphonic acid.	7 kg

15

In a second series of tests with the additives, silicate mud of the following composition was used:

- 1000 ml sea water (base)
- 20 131 g Na silicate, a solution of 14% NaOH and 27% SiO<sub>2</sub> (shale inhibitor)
- 117.5 g KCl (shale inhibitor, weighting agent)
- 20 g Polyanionic cellulose (filtrate reducer)
- 5 g Xanthan gum (viscosifier)
- 25 NaOH to adjust pH to 12.

Baseline accretion values were established as:

	simple polymer mud	9.5 kg
30	silicate mud	17.7 kg

The anti-accretion additives were tested in the silicate mud at 1% (w/v):

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Silicate mud + (1%)additive:Accretion value

	diethyl-ethylphosphonate	11.1 kg
	tri-ethyl phosphonoacetate	11.35 kg
5	tetramethyl phosphonosuccinate	9.96 kg
	phosphonosuccinic acid	10.8 kg
	2-hydroxyethyl phosphonic acid	11.4 kg

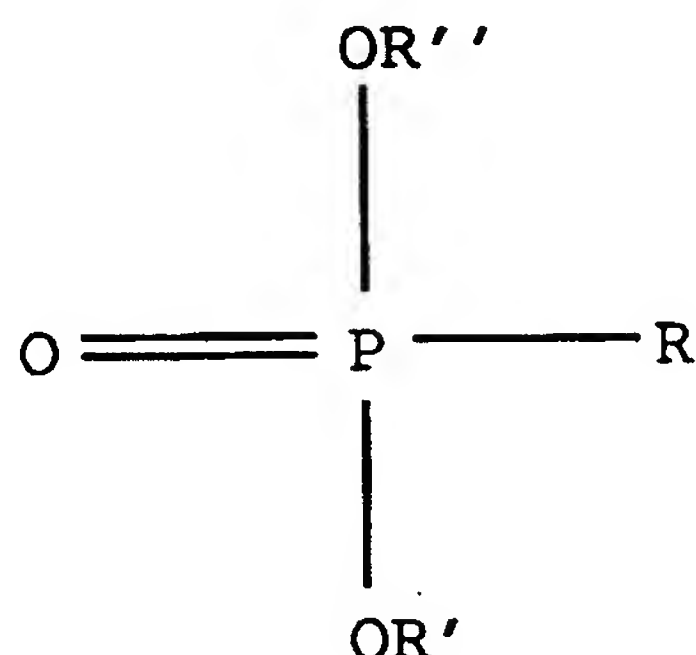
In most cases the accretion value has been reduced  
10 significantly, down to the levels of a simple polymer mud.

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## CLAIMS

1. Additive for a drilling fluid, consisting of a compound in accordance with the formula

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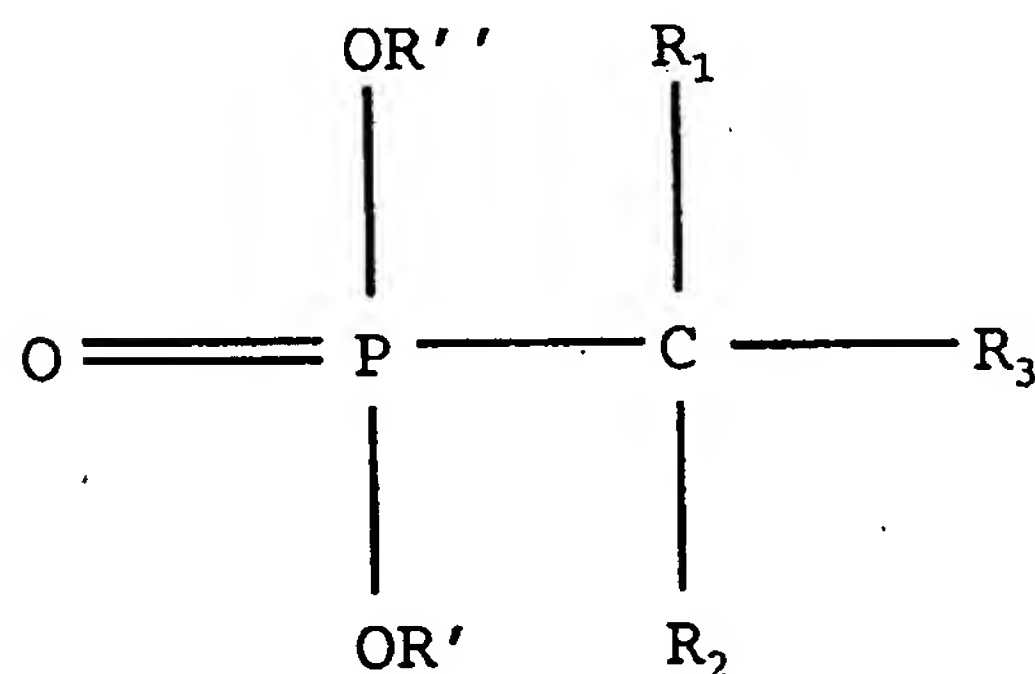
wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

10

2. The additive of claim 1, wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C or O.

3. The additive of claim 1, consisting of a compound in accordance with the formula

15

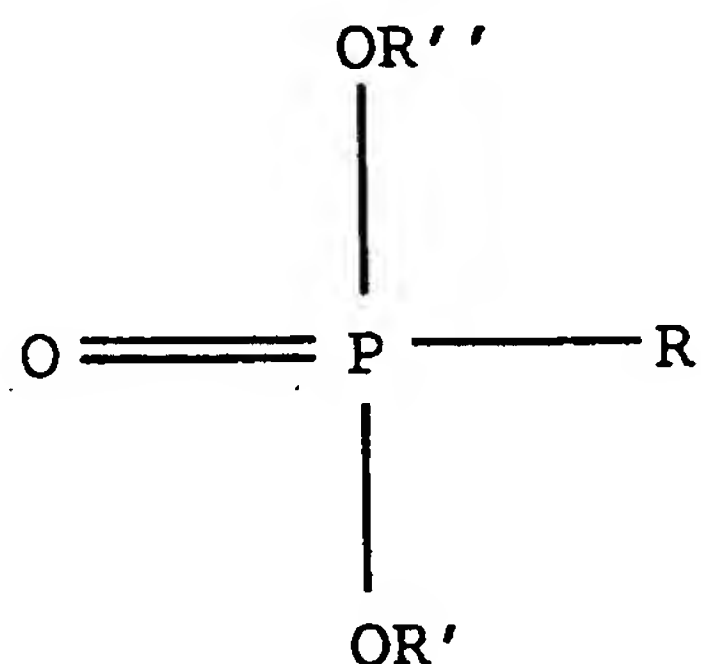


20

wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

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4. The additive of claim 3, wherein  $R_1$ ,  $R_2$  and  $R_3$  are radicals exclusively containing H atoms or combinations of H, C or O.
- 5 5. The additive of claim 1, based on a phosphor derivative of the succinic acid.
6. The additive of claim 1, based on a short chain phosphorylated hydrocarbon.
- 10 7. Drilling fluid comprising an additive in accordance with claim 1.
8. The drilling fluid of claim 5, comprising an additive in accordance with claim 1 in a concentration of up to about 10% weight by volume.
- 15 9. A drilling fluid comprising water as base component;  
a viscosifying agent to increase the viscosity of the fluid;  
a filtrate reducing agent;  
a weighting agent to adjust the density of the fluid; and  
an additive for a drilling fluid, consisting of a compound in accordance with the formula
- 20
- 25



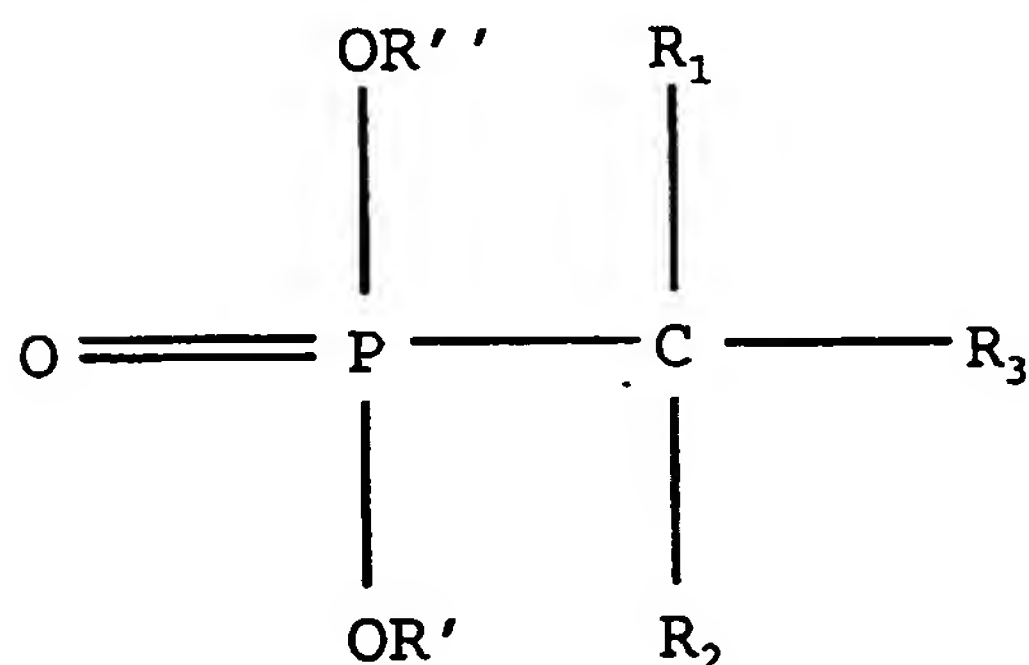
wherein  $R$ ,  $R'$  and  $R''$  are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

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10. The drilling fluid of claim 9, wherein R, R' and R'' are radicals exclusively containing H atoms or combinations of H, C or O.

5

11. The drilling fluid of claim 9, wherein the additive consists of a compound in accordance with the formula



10

wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are radicals exclusively containing H atoms or combinations of H, C, O or P atoms up to a maximum of 100 atoms.

15

12. The drilling fluid of claim 11, wherein R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are radicals exclusively containing H atoms or combinations of H, C or O.

- 20 13. The drilling fluid of claim 9, further comprising a shale swelling inhibition agent.

14. The drilling fluid of claim 13, wherein the shale swelling inhibition agent comprises phosphate- or silicate-based compounds.

25

15. Method of preventing accretion of cuttings in a borehole, said method comprising the step of adding to a drilling fluid

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an additive in accordance with claim 1 prior to or during a drilling operation.

16. The method of claim 15, wherein the additive is added in a  
5 concentration of up to about 10% weight by volume of the  
drilling fluid.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 99/00298

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 44 04 219 A (BAYER AG) 17 August 1995 see page 2, line 1 - line 8	1-8
Y	see page 2, line 31 - page 3, line 42; example 1	8,9
X	GB 2 293 373 A (ALLBRIGHT AND WILSON) 27 March 1996 see page 2, line 6 - page 3, line 7	1,3,5-8
Y	see page 6, line 15 - line 17; claims 1-3,6-9; example 2	8,9
A	DE 17 19 428 A (MONSANTO CO) 1 February 1973 see page 3, line 1 - page 4, line 3 see page 13, line 12 - page 14, line 23	1-9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 146 245 A (HENKEL) 19 March 1969 see page 1, line 9 - line 21 see page 2, line 43 - line 54	1-9



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